Reduction Equilibria of Iron Oxides. III : Measurement of the Equilibrium of the Reaction, FeO(1)+CO=Fe(1)+CO_2

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Reduction Equilibria of Iron Oxides. III
Measurement of the Equilibrium of the Reaction, $FeO(l) + CO = Fe(l) + CO_2$

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Synopsis

The author measured the equilibrium of the reaction, $FeO(l)+CO=Fe(l)+CO_2$, at the range from 1,530°C to 1,670°C, and the following equation was obtained as the temperature function of the equilibrium constant:

$$\log K_{CO-CO_2} = \log \frac{p_{CO_2}}{p_{CO}} = \frac{4,159}{T} - 3.24. \qquad (a)$$

Then, the author calculated the equilibrium constant of the reaction, $FeO(l)+H_2=Fe(l)+H_2O$, from the equation (a) and the equilibrium constant of the water gas reaction, and the following equation was obtained as the temperature function of $\log K$:

$$\log K_{H_2-H_2O} = \log \frac{p_{H_2O}}{p_{H_2}} = \frac{2.757}{T} - 1.89. \qquad (b)$$

Finally, the author calculated the dissociation pressure of molten FeO and the following equation was obtained as the temperature function of P_{O_2}:

$$\log P_{O_2}^{\frac{1}{2}} = -\frac{17,908}{T} + 7.41. \qquad (c)$$

I. Introduction

Many studies have been made on the equilibrium of the reaction, $FeO(S)+CO=Fe(S)+CO_2$ at the temperatures below 1,100°C.

The author already had studied the equilibrium of the reaction, $FeO(l)+CO=Fe(s)+CO_2$ at the range from 1,370°C to 1,520°C and reported the results in the previous paper with the experimental data at the range from 1,093°C to 1,427°C of Murpy, Wood and Jominy.(1)

Further, above the melting point of δ-iron saturated with oxygen, the following reaction proceeds:

$$FeO(l)+CO=Fe(l)+CO_2.$$

Schenck(2) already calculated the equilibrium constant of this reaction from the equation in my 2nd report and the mean value of heat of fusion of δ-iron, and proposed the following equation as the temperature function of $\log K$ of this reaction:

$$\log K_{CO-CO_2} = \log \frac{p_{CO_2}}{p_{CO}} = \frac{27,900}{4.573\,T} - 4.33. \qquad (1)$$

This equation was calculated only thermodynamically, but has never been checked experimentally, so the author measured the relation of equilibrium of this reaction at the range from 1,520°C to 1,670°C.

(1) D. W. Murphy, W. P. Wood and W. E. Jominy, Trans. Am. Soc. Steel Treat. 19 (1932), 4.
(2) H. Schenck, Physik. Chem. Eisenhüttenproz., 1 (1932) 141, 292.

II. Experimental apparatus

Fig. 1 shows the outline of the experimental apparatus. This apparatus was an improvement over the one reported in the 2nd report.

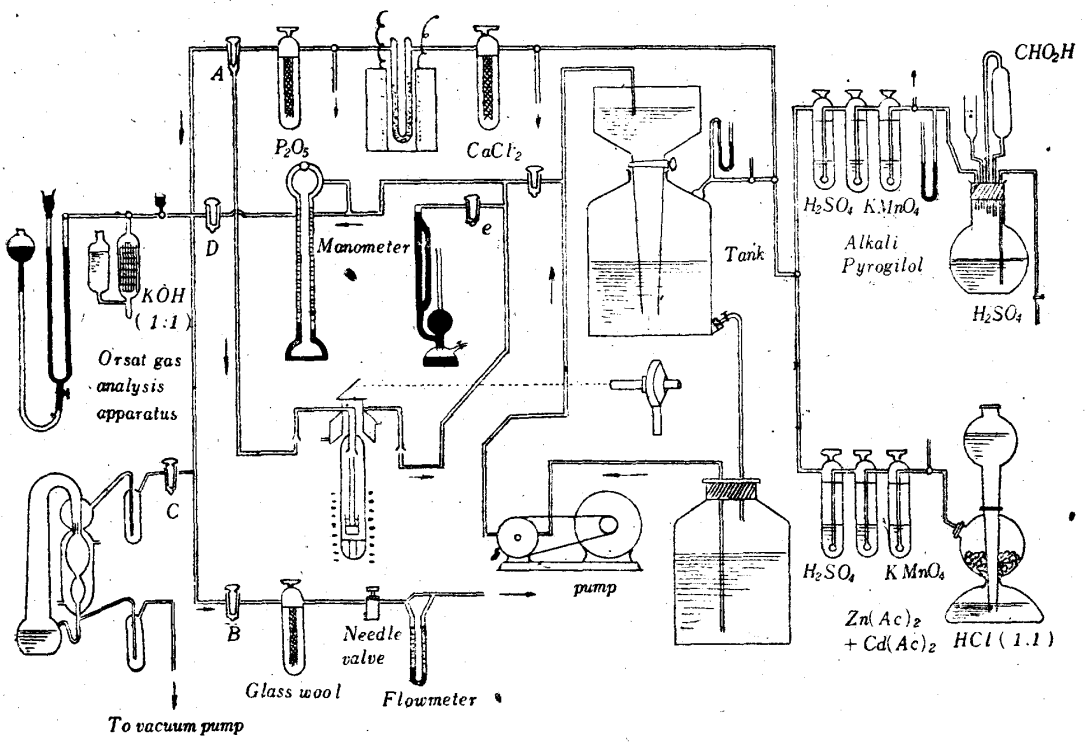

Fig. 1 Experimental apparatus.

Pure CO gas circulated in the apparatus in the previous experiment, but in this experiment the mixture of CO and CO_2 flowed at the rate of 100 cc/min through the dust catcher which was filled with glass wool, needle valve and the flow meter.

III. Sample and melting crucible

A piece of armco iron was used as a sample. Its dimension was 15 mm ϕ × 20 mm and its weight was about 25 g. The analytical result was as follows:

C (%)	Si (%)	Mn (%)	P (%)	S (%)
0.03	0.02	0.06	0.015	0.02

The crucible was made of pure magnesia (Pharmacopocia Japonia) in the laboratory.

IV. Procedure in experiment

CO gas was produced by dropping the formic acid into the conc. H_2SO_4 heated at 100~120°C.

Oxygen and moisture in CO gas were removed by passing through the alkali pyrogallol solution and the conc. H_2SO_4. Then, the gas was kept in the tank. CO_2 gas was produced from marble and HCl (1:1) in the Kipp's apparatus and

cleaned with $KMnO_4$ solution (prepared by dissolving 1 g of $KMnO_4$ and 10 g of Na_2CO_3 in H_2O 100 cc), the mixed solution of zinc acetate and cadmium acetate (prepared by dissolving 40 g of zinc acetate and 10 g of cadmium acetate in H_2O 100 cc, and 30 cc of glacial acetic acid, then dilute to 1,000 cc) and the conc. H_2SO_4, and finally reserved in the gas tank with fluid paraffin.

The mixture of CO and CO_2 gases in the tank was led into the Orsat apparatus or the reaction tube, by passing it through the $CaCl_2$ drying tower, metallic copper heated at 400°C, P_2O_5 drying tower and adjusting cock A.

In order to obtain a given gas composition before the measurement, gas analyses were repeated by adding CO or CO_2 alternatively in the tank.

Magnesia crucible which contained the iron sample was protected by the porcelain Tamman tube and charged in the reaction tube. After the reaction tube was set into the apparatus, cocks A and B were closed, and the apparatus was evacuated by means of mercury diffusion pump and rotary vacuum pump. When the apparatus attained the high vacuum, cock C was closed and cock A was opened into the path, connect to the reaction tube and the gas flowed slowly, while U tube manometer was watched: then cocks C and D were opened and the gas flowed continuously at the rate of 100 cc/min.

Iron sample was heated slowly in the high frequency induction furnace and maintained at various temperatures ranging from 1,520°C to 1,670°C under the gas of various composition.

Whether oxide film was formed or not during the melting was inspected by observing the image of the molten iron, which was reflected on the mirror set on the cap of reaction tube through the cobalt glass.

The measurements of temperature were made by means of the optical pyrometer which had been calibrated previously by the melting point of armco iron.

The iron oxide, which was formed under atmosphere richer in CO_2 than the equilibrium gas composition, revealed itself as a drop at first, then grew into a ring along the inner wall of crucible. The centre of molten iron was exposed until the end, in order that the measurement of temperature might be easy.

As CO_2% in the gas approached the equilibrium value, the amount of oxide film was decreased. Thus in this experiment, the formation of iron oxide was recognized in 40 min after the melting of sample under almost equilibrium gases composition.

A given gas composition would be considered as the more reducing gas than the equilibrium composition, when the sample was melted at a given temperature for 60~70 min and oxide was not detected.

V. Experimental results

Table 1 shows the experimental results. The results of gas analyses are applicable to the mean values before and after measurements. The experimental results obtained by plotting the melting temperature against CO % are shown in Fig. 2.

Table 1 Experimental results.

No. of experiments	Equilibrium temp. T°C	T°K	Time in min	Gas composition CO%	CO_2%	$K=\frac{p_{CO_2}}{p_{CO}}$	log K	Oxidizing or reducing	$\frac{1}{T}\times10^4$
2	1,590	1,863	10	83.9	16.1	0.191,9	−0.717,0	O	5.37
3	1,665	1,938	40	85.0	15.0	0.176,5	−0.753,3	O	5.16
4	1,610	1,883	60	78.8	21.2	0.269,0	−0.570,2	O	5.31
5	1,580	1,853	75	89.5	10.5	0.117,3	−0.930,7	O	5.39
6	1,530	1,803	55	91.3	8.7	0.095,3	−1.020,9	R	5.55
7	1 590	1,863	65	91.8	8.2	0.089,3	−1.049,1	R	5.37
8	1,540	1,813	62	89.9	10.1	0.112,3	−0.949,7	O	5.52
9	1,605	1,878	60	93.0	7.0	0.075,3	−1.123,2	R	5.32
11	1,660	1,933	60	94.4	5.6	0.059,3	−1.226,9	R	5.17
12	1,640	1,913	60	92.6	7.4	0.079,9	−1.097,5	R	5.23
13	1,670	1,943	60	92.7	7.3	0.078,7	−1.104,0	O	5.15
14	1,535	1,803	50	90.0	10.0	0.111,1	−0.954,3	R	5.54
15	1,520	1,793	45	88.5	11.5	0.129,9	−0.886,3	O	5.58
17	1,580	1,853	50	91.2	8.8	0.096,5	−1.025,5	R	5.39
20	1,620	1,893	35	91.7	8.3	0.090,5	−1.043,4	R	5.28
21	1,620	1,893	50	90.8	9.2	0.101,3	−0.994,5	O	5.28
22	1,560	1,833	65	89.7	10.3	0.114,3	−0.940,1	O	5.46
23	1,640	1,913	35	90.9	9.1	0.100,1	−0.999,6	O	5.23
24	1,595	1,863	60	90.6	9.4	0.103,7	−0.984,3	O	5.35
25	1,530	1,803	60	89.0	11.0	0.123,6	−0.908,0	O	5.55
26	1,625	1,898	50	91.7	8.3	0.090,5	−1.043,4	R	5.27
27	1,545	1,818	60	90.0	10.0	0.111,1	−0.954,3	R	5.50
28	1,570	1,843	55	90.5	9.5	0.105,0	−0.978,8	O	5.43

In the figure, ○ shows the results in which the oxide formation were not recognized until the end, that is, the cases in which the melting was performed under the gas richer in CO than the equilibrium gas composition and × shows the results in which oxide formation was recognized, that is, the cases in which melting was performed under the gas richer in CO_2 than the equilibrium.

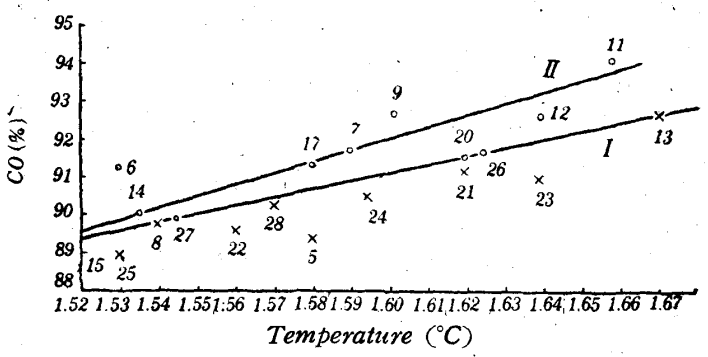

Fig. 2 Relation between melting temperature and CO% in gas
(I) Values observed by Sanbongi
(II) Values calculated by Schenck
○ Reducing × Oxidizing

Therefore, the true equilibrium gas composition should lie between × and ○.

If a straight line is so drawn as to divide × and ○ in both fields, the line should show approximately the relation between the equilibrium gas composition and the temperature. As is seen from such a line in Fig. 2, experiments No. 8, 27, 28, 20, 26 and 13 occupied almost boundary line. Therefore, this line was considered to represent the relation between CO % and temperature in the equilibrium state. In Fig. 2 the values calculated by Shenck were also plotted for comparison.

Furtheremore, Fig. 3 was obtained by calculating p_{CO_2}/p_{CO} from each experimental results and plotting log p_{CO_2}/p_{CO} against $1/T$.

As the gas compositions of No. 13, 26, 20, 28, 27 and 8 were considered to be

almost equilibrium gas compositions from the previous explanation, values of p_{CO_2}/p_{CO} from these results show the equilibrium constant at each temperature.

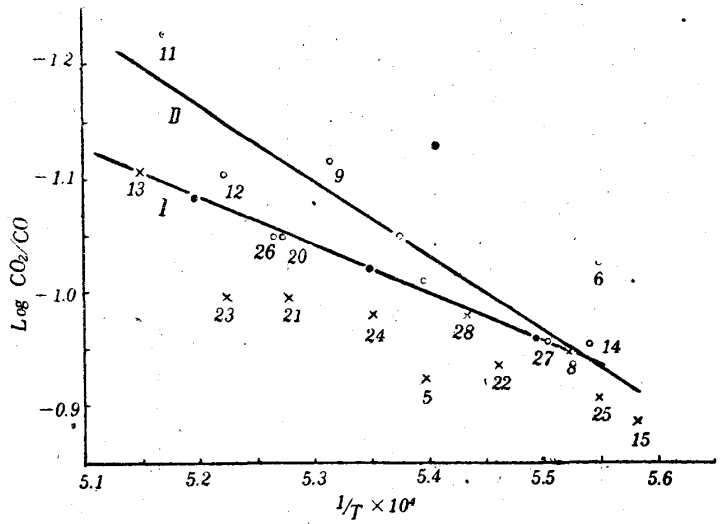

Fig. 3 Relation between log CO_2/CO and $1/T$
I Observed values, log $K=4{,}159/T-3.24$
II Values calculated by Schenck
○ Reduding ● Cal. from eq. 2 × Oxidizing

Calculating the temperature function of the equilibrium constant from these results by the method of least square, the following equation was obtained:

$$\log K_{CO-CO_2}=\log\frac{p_{CO_2}}{p_{CO}}=\frac{4{,}159}{T}-3.24\ , \qquad (2)$$

$$\Delta F^\circ=-4.578{,}7\,T\log K=-19{,}042+14.838\,T. \qquad (3)$$

VI. The equilibrium of the reaction, $FeO(l)+H_2=Fe(l)+H_2O$.

Denoting the equilibrium constant of the reaction, $FeO(l)+CO=Fe(l)+CO_2$, and water gas reaction by K_{CO-CO_2} and K_w, the equilibrium constant $K_{H_2O-H_2}$ of the reaction $FeO(l)+H_2=Fe(l)+H_2O$ becomes as follows:

$$K_{H_2O-H_2}=\frac{p_{H_2O}}{p_{H_2}}=K_w\times K_{CO-CO_2}\,.$$

Schenck proposed the following equation as the temperature function of this reaction:

$$\log K_{H_2O-H_2}=\log\frac{p_{H_2O}}{p_{H_2}}=\frac{23{,}200}{4.573\,T}-3.21\,. \qquad (4)$$

The equilibrium constant of water gas reaction was given very accurately by Neuman and Köhler[3] as follows:

$$CO_2+H_2=CO+H_2O,$$

$$\log K_w=\log\frac{p_{CO}\cdot p_{H_2O}}{p_{CO_2}\cdot p_{H_2}}=-\frac{2{,}190}{T}-0.201\log T-0.393\times10^{-3}T+5.46\times10^{-8}T^2+2.979\,. \qquad (5)$$

Calculating K_{CO-CO_2} and K_w from the equation (2) and (5), values of $K_{H_2O-H_2}$ can be calculated at several temperatures. Table 2 gives these calculated values.

(3) E. Neuman and G. Köhler, Z. Elektrochem., 34 (1928), 218.

Table 2 Calculated value of $K=p_{H_2O}/p_{H_2}$ at each temperature.

T°C	T°K	$K=\frac{p_{CO_2}}{p_{CO}}$	K_w	$K=\frac{p_{H_2O}}{p_{H_2}}$	$\log K=\log\frac{p_{H_2O}}{p_H}$
1,550	1,823	0.109,8	3.867	0.424,5	−0.372,1
1,600	1,873	0.095,4	4.052	0.386,5	−0.412,8
1,650	1,923	0.083,5	4.231	0.353,3	−0.451,8

The temperature function of log $K_{H_2O-H_2}$ becomes as follows:

$$\log K_{H_2O-H_2}=\log\frac{p_{CO}\cdot p_{H_2O}}{p_{CO_2}\cdot p_{H_2}}$$

$$=\frac{2,758}{T}-1.89\ . \qquad (6)$$

Plotting $K_{H_2O-H_2}$ against $1/T$ at several temperatures from the equation (6), curve I in Fig. 4 was obtained. In Fig. 4, curve II calculated from the equation (4) is also shown for comparison.

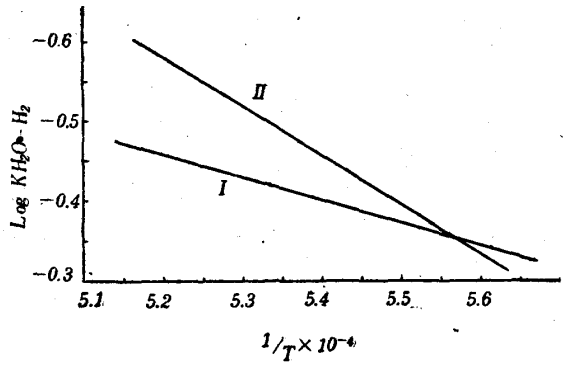

Fig. 4 Relation between log $K_{H_2O-H_2}$ and $1/T$
I Values observed by Sanbongi log $K_{-H_2H_2O}=2,758/T-1.89$
II Values calculated by Schenck

VII. The equilibrium of the reaction, $FeO(l)=Fe(l)+\frac{1}{2}O_2$

The dissociation pressure of this reaction can be calculated from the equilibrium constant of the reaction, $FeO(l)+CO=Fe(l)+CO_2$ and the dissociation constant of CO_2 by the following formula:

$$P_{O_2}^{\frac{1}{2}}=D_{CO_2}/K_{CO-CO_2}\ .$$

The temperature function of dissociation constant of CO_2 was given by Wartenberg[4] as follows:

$CO_2=\frac{1}{2}O_2+CO$,

$$\log D_{CO_2}=\log\frac{p_{CO}\cdot p_{O_2}^{\frac{1}{2}}}{p_{CO_2}}=-\frac{14,750}{T}+1.375\log T-0.607,5\times10^{-3}T$$

$$+0.675\times10^{-7}T^2+11.0 \qquad (7)$$

From the equation (2) and (7), values of K_{CO-CO_2} and D_{CO_2}, and then $P_{O_2}^{\frac{1}{2}}$ can be calculated at several temperatures. Table 3 gives these calculated values at several temperatures.

Calculating the temperature function of log $P_{O_2}^{\frac{1}{2}}$ from these data, the following equation was obtained:

$$\log P_{O_2}^{\frac{1}{2}}=\frac{-17,908}{T}+7.41 \qquad (8)$$

(4) H. V. Warterberg, Z. Phys. Chem., 58 (1906), 548.

Table 3 Calculated value of $P_{O_2}^{\frac{1}{2}}$ at each temperature.

T°C	T°K	log D_{CO_2}	log p_{CO_2}/p_{CO}	log $P_{O_2}^{\frac{1}{2}}$
1,550	1,823	−3.397,3	−0.959,4	−2.437.9
1,600	1,873	−3.177,8	−1.020,3	−2.157,5
1,650	1,923	−2.973,1	−1.078,1	−1.895,0

Summary

The author measured the equilibrium of the following reaction at the temperature range from 1,530°C to 1,670°C.

$$FeO(l)+CO=Fe(l)+CO_2$$

And as the temperature function of log K_{CO-CO_2}, the following equation was obtained:

$$\log K_{CO-CO_2}=\frac{4,159}{T}-3.24 .$$

Then the author calculated the equilibrium constant of the reaction, $FeO(l)+H_2=Fe(l)+H_2O$, and the following equation was obtained as the temperature function of log $K_{H_2O-H_2}$:

$$\log K_{H_2O-H_2}=\log\frac{p_{H_2O}}{p_{H_2}}=\frac{2,758}{T}-1.89 .$$

Finally the author calculated the dissociation pressure of the reaction, $FeO(l)=Fe(l)+\frac{1}{2}O_2$, and the following equation was obtained as the temperature function of log $P_{O_2}^{\frac{1}{2}}$:

$$\log P_{O_2}^{\frac{1}{2}}=-\frac{17,908}{T}+7.41 .$$